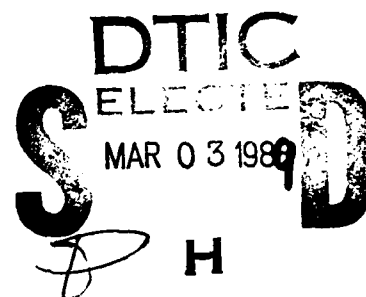e 801861

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An Investigation of the Thermal Decom-position of 1, 4-Butanediammonium Dinitrate and Selected Composites With Ammonium and Potassium Nitrates

R L McKenney, Jr
S R Struck, et al.

ENERGETIC MATERIALS BRANCH
MUNITIONS DIVISION

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This report describes the investigation of the thermal decomposition of 1,4-butanediammonium dinitrate (BDD), specifically C- and N-deuterated analogs, selected composites with ammonium and potassium nitrates, and composite N-deuterated analogs. Analytical techniques used for this work were differential scanning (DSC) and accelerating rate calorimetry, thermogravimetry, tandem gas chromatography/mass spectrometry, high performance liquid chromatography, and deuterium labeling. Impact sensitivities, times to explosion, and critical temperatures were determined for these materials. Condensed phase induction period studies performed by using specifically deuterated BDD analogs generally displayed inverse deuterium isotope effects. While these studies did not unequivocally reveal the specific covalent bond rupture responsible for generating conditions favorable for exothermic decomposition, they did provide a direct relationship between induction period chemistry as measured by quantitative isothermal differential scanning calorimetry and macroscopic thermal sensitivity properties. The data suggested that BDD, when formulated into BAK composites, decomposes independently of the
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ammonium nitrate/potassium nitrate components by a process similar to that of pure BDD. This same decomposition process appears to control the isothermal DSC induction period of these composites as well as their times to explosion, critical temperatures and impact sensitivities.

PREFACE

This report describes an in-house program conducted by personnel of the Energetic Materials Branch (MNE), Munitions Division (MN), Air Force Armament Laboratory (AFATL), Eglin Air Force Base FL 32542-5434, under Project 2303E110. Dr Robert L. McKenney, Jr., managed the program for the Air Force Armament Laboratory. The work reported herein was conducted during the period of 1 October 1985 to 31 December 1988.

The author wishes to thank Doctors Alan P. Marchand, University of North Texas; Thomas B. Brill, University of Delaware; and Paul R. Bolduc, Energetic Materials Branch, for their helpful discussions and technical critique regarding this work. Thanks are also extended to Doctor Peter Meyer and Ms Elizabeth A. Deibler for their untiring efforts in carrying out certain aspects of the experimental portion of this work. Their participation was afforded through auspices of the Graduate Student Research and High School Apprenticeship Programs, respectively.

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SECTION I
INTRODUCTION

Organodiammonium dinitrate salts have been of interest to the explosives community as an ingredient in composite energetic materials for many years, Reference 1. In particular, 1,2-ethanediammonium dinitrate (EDD) was of interest because it forms a low-melting eutectic mixture with ammonium nitrate (AN), Reference 2. While the thermal chemistry of AN has been extensively studied, References 3-5, only minimal information is available on organodiammonium dinitrate salts. It is generally concluded that the initial step in the thermal decomposition of AN, Reference 6, and simple aliphatic ammonium nitrates, $[RNH_3]NO_3$, References 7-8, is predominantly dissociation followed by, or in conjunction with, exothermic decomposition. The initial step in the decomposition process for more complex ammonium nitrate salts, e.g., pentaerythrityltetrammonium tetranitrate (PTTN), Reference 9a, EDD, Reference 9b, and 1,4-butanediammonium dinitrate (BDD), Reference 10, was also found to be similar. The results of early thermolysis experiments with EDD show the decomposition to be autocatalytic. While the reaction residue was not fully characterized, the data suggested that both nitramine- and nitrosamine-containing compounds were formed during the EDD decomposition process, Reference 11.

This report describes the results of an investigation of the thermal decomposition of BDD that were obtained by using differential scanning calorimetry (DSC), deuterium labeling, thermogravimetric analysis (TGA), tandem gas chromatography/mass spectrometry (GC/MS), high performance liquid chromatography (HPLC), accelerating rate calorimetry (ARC), and impact and time to explosion analytical techniques. Gaseous and volatile products have been identified, and degradation steps are postulated to account for their formulation.

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SECTION II
EXPERIMENTAL PROCEDURES/RESULTS

DSC and TG analyses were performed with a DuPont Instruments 1090 Thermal Analyzer equipped with Models 910 DSC and 951 TGA plug-in modules, respectively, and a Perkin-Elmer DSC-4/Thermal Analysis Data Station System. The ARC technique was developed by the Dow Chemical Company, and ARC instrumentation is manufactured commercially by Columbia Scientific Industries Corporation. Mass spectra were acquired with a Chemical Data Systems Model 310 Concentrator and a Finnigan Model 4500 GC/MS. Infrared spectra were obtained with Perkin-Elmer Model 683 and Biorad (Digilab Division) Model FTS-50 Infrared Spectrophotometers.

TGA and DSC residues were transferred to the GC/MS from a concentrator oven at $155^{\circ}C$ with helium flow at $20\ cm^3/min$. Volatile components were concentrated on a Tenax GC trap and then flash heated to $200^{\circ}C$ to effect the transfer to the GC. A 15-meter, 0.53 mm-I.D. J & W Scientific DB-1 (methyl-silicone coating) fused quartz capillary column, programmed to $180^{\circ}C$ at $20^{\circ}C/min$, was used to separate the components. The helium carrier gas was partially removed from the GC effluent prior to reaching the MS by using an in-line jet separator.

ARC samples were heated in specially mounted 0.25-inch I.D. Pyrex glass tubes. Prior to heating, each sample was purged with high purity helium, pressurized to 23 psia and leak tested to insure that no air was present. The reaction tube was equipped with a 0.25 mm I.D. empty fused quartz capillary tube for gas sampling. Gaseous products were transferred from the ARC to the GC/MS through a 20 meter long, 0.53 mm I.D., capillary column (methyl-silicone coating) attached to a Nutech Model 320 sample injection valve. Care was taken to insure the absence of impurities and leaks during the transfer.

Anion and cation separations, respectively, were accomplished by using: a Waters Associates Model ILC-1 Chromatograph equipped with an IC-PAK A column and a Waters Associates Model ILC-2 Chromatograph equipped with

IC-PAK C column. Samples were filtered through Water Associates Sep-Pak C18 cartridges prior to injection into the chromatograph to remove nonionized organic components.

Samples (1.55+0.05mg) for isothermal DSC experiments were weighed into standard aluminum pans (Perkin-Elmer part number 219-0062), transferred to a Vacuum Atmospheres Company inert atmosphere box, and stored under vacuum (10 microns) for 24 hours prior to sealing. Some sample pans were sealed hermetically under a water/oxygen-free nitrogen atmosphere while others were sealed in air.

Impact data were obtained with a Bureau of Mines Model No. 2 Impact Device. The composites tested were dried under vacuum at 50-60°C for several hours and then ground and stored in a desiccator. The materials were not sieved prior to testing. Each powdered sample was impacted on Norton coated abrasive paper of 180 grit (FSN 5350-271-7930). Twenty-five to thirty samples were used for each complete test. Time to explosion test apparatus and procedure have been described elsewhere, Reference 12.

1. DYNAMIC TGA EXPERIMENT

BDD (20 mg) was heated in a TG analyzer at a rate of 5°C/min. A AgCl disposable IR plate was exposed to the furnace exhaust port effluent during the temperature range 200-215°C. Total weight loss during the exposure period was approximately 40 μ g. The spectrum obtained from the material collected on the IR plate contained strong, broad absorption bands at 3100 and 1380 cm^{-1}. Other weak bands were observed at 2410, 1750, 1580, and 830 cm^{-1}. AN exhibits characteristic absorptions at 3125 (s,br), 3020 (sh), 2380 (vw), 1750 (vw), 1360 (vs,br), 830 (w) and 720 (vw) cm^{-1}.

2. ISOTHERMAL TGA EXPERIMENT I

BDD (61 mg) was heated at 230°C for 400 min, during which time the sample lost 66 percent of its original weight. Volatile material was deposited on the cooler portion of the furnace tube that extended beyond the heater a white

solid being collected nearest the heater. The IR spectrum of the solid
exhibited absorptions at 3000 (s, br), 2000 (w, d), 1740 (m), 1615 (s), 1590
(sh), 1505 (vw), 1470 (vw), 1345 (vs, br), 1105 (w), 1030 (w), 910 (w), 880
(w), 825 (w), 755 (w) and 720 (w) cm^{-1}. Pure BDD (KBr)
exhibits bands at 3010 (s, br), 2010 (w), 1980 (w, br), 1745 (w), 1620 (m),
1590 (sh), 1510 (vw), 1465 (vw), 1350 (vs, br), 1105 (m), 1025 (w), 910 (m),
875 (m), 830 (m), 755 (w) and 725 (w) cm^{-1}. The prominent absorption at
1105 cm^{-1} is characteristic of BDD. The IR spectrum of the brown viscous
liquid that was collected beyond the solid showed no evidence of BDD.

3. ISOTHERMAL TGA EXPERIMENT II

BDD (28 mg) was heated at 229°C for 840 minutes, during which time the
sample lost 84 percent of its original weight. A brown viscous effluent was
deposited on the furnace tube. The viscous effluent was analyzed by chemical
ionization (CI) mass spectrometry using methane (CH$_4$) as the reagent gas.
The GC/MS (CI/CH$_4$) reconstructed ion chromatogram (RIC) that was obtained for
the viscous effluent revealed the presence of four relatively minor products
(I, II, III, IV) and one major product (V) (See Figure 1). As an aid to
interpretation, spectra were also obtained using (1) CD$_4$ reagent gas and (2)
products from deuterium labeled salts, Reference 13. Products III, IV, and V
were identified as being 1,3-dinitratobutane (1,3-DNBu), 1,4-dinitratobutane
(1,4-DNBu) and N-nitrosopyrrolidine (PNSA), respectively. Products I and II
were not identified. Mass spectral results are summarized in Table 1.

4. ISOTHERMAL DSC EXPERIMENT

BDD (2.0 mg) was heated in a partially evacuated glass bulb at 210°C
until the liquid at the bottom of the bulb began to bubble and darken. The
volatile materials that emanated from the bulb were transferred to the mass
spectrometer. The RIC, shown in Figure 2, is composed of four significant
products (III, IV, V and X) and 12 minor products (I, VI, VII, VIII, IX,
XI, XII, XIII, XIV, XV, XVI and XVII). The mass spectra (CI/CH$_4$) associated
with compounds I, III, IV and V of Figure 2 are identical to those obtained
from the similarly labeled RIC peaks shown in Figure 1.

The EI and CI mass spectral fragment patterns for product X are shown in Tables 2 and 3, respectively. Also included are the predicted fragment patterns for 4-nitrato-1-butene and its expected deuterated analogs.

Minor products for which sufficient mass spectral data to support tentative identification could be obtained are listed in Table 4. The identification of compounds VIII (tetrahydrofuran) and XV (N-nitropyrrolidine), as shown in Figures 3 and 4, respectively, is supported by EI mass spectral data that closely matches that of authentic samples.

The mass spectral (CI/CH_4) pattern associated with compound XIV exhibits a base ion at $\underline{m/e}$ = 101 and ions of low to moderate abundance at $\underline{m/e}$ = 73, 76 (CH_2NO_3), 87, 118 ($M-NO_3$) and 181 ($M + H$). This suggests yet another dinitratobutane (DNBu) isomer, the most logical choice being the 2,3-isomer.

A summary of the identified condensed phase reaction products from the DSC experiment is shown in Table 5. The remaining nine (9) minor products (I, VI, VII, IX, XI, XII, XIII, XVI and XVII) cannot be characterized sufficiently with the available spectral data for tentative identification.

5. ION CHROMATOGRAPHY EXPERIMENT

Several 2.0 mg samples of BDD were sealed in partially evacuated glass bulbs and heated to 190°C. Samples were viewed by using a microscope and were removed from the hot stage at various stages of decomposition as subjectively determined by discoloration. The samples were analyzed within 10 minutes after removal. The results of chromatographic analysis are shown in Table 6.

6. ARC EXPERIMENT

BDD, 200 mg, was heated in an ARC reaction vessel at 176-184°C for 266 minutes. No significant self-heating occurred during this time; hence, this time is considered to be within the induction period. Aliquots of the helium atmosphere above the molten sample were removed at 30-minutes intervals and then analyzed by GC/MS. The gases found (N_2, NO, N_2O, CO_2, and H_2O) were all

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evolved at rates between 0.98 and 2.0 x 10^{-3} mole/min. Nitrogen dioxide could not be detected reliably from either sample aliquot or standard gas; however, other researchers have verified its presence, Reference 14. The total nitrogen (N) evolved, calculated from the total amounts of N_2, NO, and N_2O evolved during the course of the experiment, was 0.10 percent of the total nitrogen (N) available from BDD.

Another ARC experiment was carried out under conditions similar to those described above. Analysis of the product mixture using GC/MS revealed the presence of ethene, propene, 1,3-butadiene and carbon monoxide, in addition to the products shown above. GC retention times and mass spectral patterns associated with these compounds corresponded with those obtained from authentic samples.

7. IMPACT EXPERIMENTS

Impact sensitivity experiments were carried out with four BAK and one BAK-d_x (11 mole percent AN) composites by using a 2.5 kg weight. The results are compared with those previously acquired with BDD and are presented in Table 7.

8. TIME TO EXPLOSION EXPERIMENTS

Time to explosion tests were carried out on 40 mg samples of BDD, its N-deuterated analog, various BAK composites and their N-deuterated analogs. Times to explosion versus temperature curves are shown in Figure 5 and versus critical temperatures are shown in Table 8.

9. DSC DEUTERIUM ISOTOPE EFFECT (DIE) STUDIES

BDD-1,1,4,4-d_4 and BDD-2,2,3,3-d_4 were prepared according to the procedures described elsewhere, Reference 13. N-deuterated BDD and BAK (11 mole percent AN) were prepared by dissolving approximately 1 g of the original salt/mixture in 5 ml of D_2O. The resulting solution was stirred for 30 minutes and then evaporated to dryness. The procedure was repeated, and the resulting product was then dried to constant weight in vacuo at 50°C and

stored in an inert atmosphere box. Thermolysis experiments were carried out with the sample in the liquid phase and are characterized by an induction period that preceded acceleratory exothermic decomposition. DIE results obtained in both air and nitrogen atmospheres are shown in Table 9.

10. CUMULATIVE INDUCTION PERIOD (DSC) STUDY

Cumulative thermolysis experiments were carried out with BDD at 190°C in air. The sample was removed from the heat source and quenched after a timed fraction of the induction period had occurred. The sample was then reheated to 190°C and held until the end of the induction period. This experiment was repeated two more times. The average of the combined times for each experiment was compared with the average induction time obtained from six experiments carried out at the same temperature. The results are shown in Table 10.

11. THERMOLYSIS OF PYRROLIDINIUM NITRATE (PN)

PN was prepared by reacting pyrrolidine with concentrated nitric acid in a 1:1 mole ratio in a manner similar to that described by McKenney, Reference 15. The tan product was a viscous oil to semisolid at room temperature; IR (neat) 3000 (vs, br), 1750 (w), 1709 (m), 1613 (m), 1375 (vs, br), 1030 (s), 912 (m), 880 (w), 826 (s), 716 (w) cm^{-1}; ^{1}H NMR (DMSO-d$_6$) 1.9 (m, 4H), 3.2 (t, 4H), 8.9 (br s, 2H); mass spectrum (70 eV), m/e (relative intensity): (no molecular ion), 71 (9.3), 70 (12.8), 46 (24.9), 43 (100), 42 (17.4), 41 (15.3), 39 (9.8), 30 (19.8), 27 (11.2).

PN (0.1 mg) was introduced into the GC/MS through a concentrator oven as described previously. The resulting RIC, shown in Figure 6, is characterized by one major product. The mass spectrum (CI/CH$_4$) of this product is identical to that of product V from the decomposition of BDD and is identified as being N-nitrosopyrrolidine (PNSA).
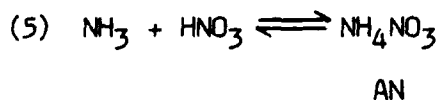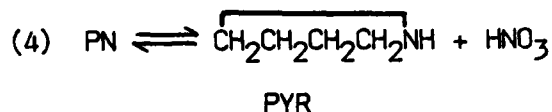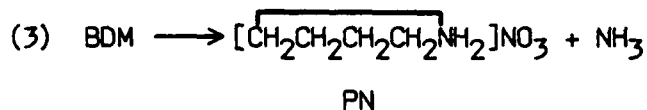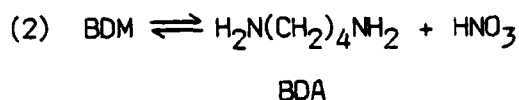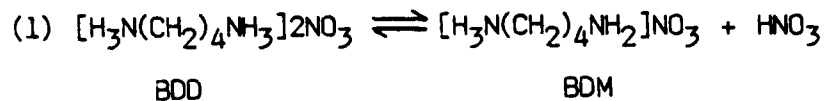
SECTION III
DISCUSSION

The data generated from this study suggest that the BDD induction period is characterized by competitive, endothermic reactions that create conditions that ultimately lead to exothermic decomposition. Isothermal DSC experiments with BDD in vented sample pans are typified by subtle endotherms of long duration followed by rapid exothermic decomposition. Loss of volatiles, thought to occur during this endothermic period, was confirmed by isothermal TGA at a temperature as low as 180°C in a flowing N_2 atmosphere, Reference 16. BDD has been shown previously to completely dissociate into 1,4-butanediamine (BDA) and HNO_3 at elevated temperature in high vacuum with no other decomposition reactions apparent, Reference 10. The presence of BDD in the effluent from isothermal TGA experiment I suggests that dissociation/ association also occurs to some small extent at atmospheric pressure. The shape of relatively low temperature TGA curves at atmospheric pressure, however, suggests reactions other than dissociation are occurring. While AN was not detected in the effluent from isothermal TGA experiments, the effluent from a specific time/temperature period of a dynamic TGA experiment yielded a white solid that produced an IR spectrum that indicated the presence of AN. Even though the total weight loss over this period was minimal, the presence of AN indicates that C-N bond rupture occurs early in the BDD decomposition process at atmospheric pressure. The detected AN is thought to result from the reaction of NH_3 with HNO_3 in the vapor phase, Reference 14.

In an effort to identify more of these early products, BDD was decomposed in a sealed bulb under partial vacuum at 190°C, and the reaction residue was analyzed by cation/anion chromatography. The reactions were quenched at various stages of reactivity as judged by qualitative observation of color change in the reaction residue. Very small percentages (relative to total sample reacted) of ammonium and pyrrolidinium cations were detected

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with the former being detected first. The order of appearance is consistent with the findings of Brill, Reference 14, and appear to support the existence of the following early reactions:

(1) $[H_3N(CH_2)_4NH_3]2NO_3 \rightleftharpoons [H_3N(CH_2)_4NH_2]NO_3 + HNO_3$

      BDD   BDM

(2) $BDM \rightleftharpoons H_2N(CH_2)_4NH_2 + HNO_3$

                        BDA

(3) $BDM \longrightarrow [\overline{CH_2CH_2CH_2CH_2NH_2}]NO_3 + NH_3$

                        PN

(4) $PN \rightleftharpoons \overline{CH_2CH_2CH_2CH_2NH} + HNO_3$

                        PYR

(5) $NH_3 + HNO_3 \rightleftharpoons NH_4NO_3$

                                  AN

BDM and PN have not been directly confirmed as intermediate reaction products in the condensed phase by analysis. BDM, however, is a logical choice as a precursor to the cycloelimination reaction that leads to PYR.

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This reaction is consistent with the theoretical findings of Politzer, Reference 17, wherein a $C-NH_3^+$ bond was calculated to be weaker than a $C-NH_2$ bond; hence, the former is favored $\bigcirc$ C-N bond fission. PN, on the other hand, has been identified by Brill, Reference 14, in the aerosol above decomposing BDD, but its formation in the condensed phase does not seem likely. It is unstable above $100^{\circ}C$ at atmospheric pressure and would not be expected to be stable in the condensed phase under these experimental conditions. Based on these data, it is probably best to describe the early decomposition of BDD in terms of equations 1 through 5 plus equations 6 and 7.
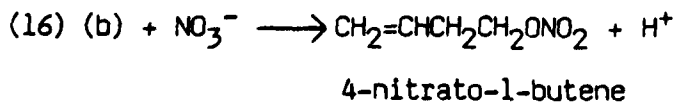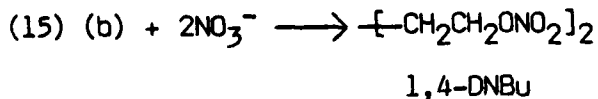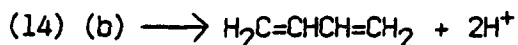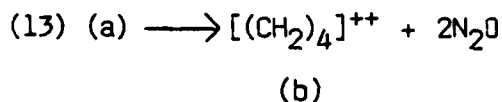
(6) BDM $\longrightarrow$ PYR + AN

(7) BDA $\longrightarrow$ PYR + NH_3
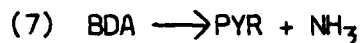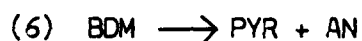
The finding of PNSA among the reaction products, coupled with the fact that PN yields significant amounts of PNSA upon thermolysis, strongly suggests that PN is formed as a transient species at some point during the early BDD thermolysis process. Subsequent decomposition of PN to form PNSA may then occur, perhaps through a dehydration reaction to form transient N-nitropyrrolidine (PNA). Small amounts of PNA have been detected in the BDD reaction products, but PNA has not been detected among the products of PN decomposition. It is postulated that PNA decomposes in a manner similar to that of dimethylnitramine, Reference 18, thereby forming PNSA as the primary decomposition product.

The presence of N_2O and N_2 in the BDD decomposition effluent suggests that transient, primary nitramine and nitrosamine functional groups may also appear during the thermolysis process. Nitrous oxide, however, may also result via degradation of AN, which has been shown to form early in the process. The degradation of relatively unstable primary nitramine and nitrosamine species in the presence of HNO_3 may also account for the presence of the three DNBu isomers. The degradation may, for example, proceed via the corresponding diazonium and diazonium oxide ions, thus leading to formation of the DNBu isomers through solvolysis/elimination reactions, Reference 19a, coupled with carbon to carbon migration of hydride ion, Reference 19b.

Based on condensed phase and gaseous products identified from BDD thermolysis effluent and residue, additional reactions are postulated to occur later in the thermal decomposition process. The decomposition chemistry occurring in molten BDD is believed to be complex; however, many of the proposed reactions shown below are presented as unimolecular and, in some cases, in a stepwise manner for purposes of clarity, Reference 20.

(8) $\quad$ PN $\longrightarrow$ $\overline{CH_2CH_2CH_2CH_2N}NO_2$ + H_2O

$\qquad\qquad$ PNA

(9) $\quad$ PNA $\longrightarrow$ $\overline{CH_2CH_2CH_2CH_2N}NO$ + other products

$\qquad\qquad$ PNSA

(10) $\quad$ BDD $\longrightarrow$ $O_2NNH(CH_2)_4NHNO_2$ + $2H_2O$

$\qquad\qquad$ BDNA

(11) $\quad$ BDNA $\longrightarrow$ $ONNH(CH_2)_4NHNO$ + other products

$\qquad\qquad$ BDNSA

(12) $\quad$ BDNA $\xrightarrow{2H^+}$ $-[-CH_2CH_2-N=N=O^+]_2$ + $2H_2O$

$\qquad\qquad\qquad$ (a)

(13) $\quad$ (a) $\longrightarrow$ $[(CH_2)_4]^{++}$ + $2N_2O$

$\qquad\qquad$ (b)

(14) $\quad$ (b) $\longrightarrow$ $H_2C=CHCH=CH_2$ + $2H^+$

(15) $\quad$ (b) + $2NO_3^-$ $\longrightarrow$ $-[-CH_2CH_2ONO_2]_2$

$\qquad\qquad\qquad$ 1,4-DNBu

(16) $\quad$ (b) + NO_3^- $\longrightarrow$ $CH_2=CHCH_2CH_2ONO_2$ + H^+

$\qquad\qquad\qquad$ 4-nitrato-1-butene

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$$(17) \quad (b) \longrightarrow \overset{+}{C}H_2CH_2\overset{+}{C}HCH_3$$

$$(c)$$

$$(18) \quad (c) + 2NO_3^- \longrightarrow O_2NO(CH_2)_2CH(ONO_2)CH_3$$

$$1,3\text{-DNBu}$$

$$(19) \quad (b) \longrightarrow CH_3\overset{+}{C}H\overset{+}{C}HCH_3$$

$$(d)$$

$$(20) \quad (d) + 2NO_3^- \longrightarrow \text{-}[\text{-}CH(ONO_2)CH_3]_2$$

$$2,3\text{-DNBu}$$

$$(21) \quad BDNSA \xrightarrow{2H^+} \text{-}[\text{-}CH_2CH_2\text{-}N{=}\overset{+}{N}]_2 + 2H_2O$$

$$(e)$$

$$(22) \quad (e) \longrightarrow (b) + 2N_2$$

$$(23) \quad (b) + 2NO_3^- \longrightarrow 1,4\text{-DNBu}$$

$$(24) \quad (c) + 2NO_3^- \longrightarrow 1,3\text{-DNBu}$$

$$(25) \quad (d) + 2NO_3^- \longrightarrow 2,3\text{-DNBu}$$

$$(26) \quad BDD \xrightarrow{2H^\cdot} \text{-}[\text{-}CH_2\overset{\cdot}{C}HNH_3]_2 2NO_3$$

$$(f)$$

$$(27) \quad (f) \longrightarrow 2[CH_2{=}CHNH_3]NO_3 \longrightarrow H_2C{=}\overset{\cdot}{C}H + \overset{\cdot}{N}H_3NO_3$$

$$(g) \qquad\qquad (h)$$

$$(28) \quad (h) \longrightarrow H_2C{=}CH_2 + 1,3\text{-butadiene}$$

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Condensed phase kinetic deuterium isotope effect (KDIE) studies have been used successfully to determine the reaction mechanisms associated with the thermochemical decomposition of energetic materials, References 21-25. The materials previously studied include octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexahydro-1,3,5-trinitro-s-triazine (RDX), 2,4,6-trinitrotoluene (TNT) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). The present study has sought to use the KDIE to elucidate the chemical reaction mechanisms associated with the induction period of the isothermal decomposition curve for molten BDD. The induction period is defined as the time elapsed from t=0 at isothermal temperature until the initial deflection of the exothermic acceleratory phase from the horizontal baseline. It is believed that the chemical reactions that occur during the induction period result in the accumulation of a threshold concentration of materials which catalytically initiate exothermic decomposition. This supposition is supported by the results of the cumulative induction period study where it was demonstrated that the induction period is afforded a memory. While a rate constant, k, cannot be determined for the induction period, direct measurement of induction times, t, can be obtained from isothermal DSC experiments. It has been suggested, Reference 22, that the induction time is inversely proportional to the rate constant

$$\frac{k_h}{k_d} = \frac{t_d}{t_h}$$

where t_d is the induction time for a specifically deuterated BDD and t_h is the induction time for BDD.

In the present study, deuterated analogs of BDD were prepared in which the deuterium atoms were selectively placed around the C-N bonds, since calculational data suggest that this bond is the most likely to rupture. Assuming that C-N bond rupture is involved in the transition state and taking into consideration the selective placement of deuterium atoms in the

substrate, the observed inverse deuterium isotope effect for the BDD-1,1,4,4-d_4 and the near-unity t_d/t_h value for the N-deuterated salt were unexpected. A cycloelimination reaction is believed to be the rate determining step leading to conditions favorable for initiation of the acceleratory phase of the decomposition process. The following structure is thought to be representative of the probable transition state associated with this reaction:
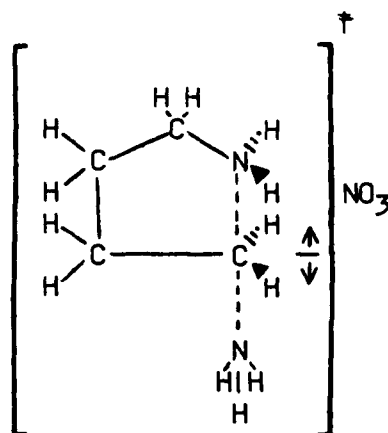
Inhibition of the C-H out-of-plane bending motion of the central carbon atom can then account for the results from BDD-1,1,4,4-d_4 and BDD-N,N,N',N',N'-d_6, Reference 26 and 27.

Time to explosion experiments represent a thermal explosion event carried out under conditions more hostile than those associated with quantitative laboratory isothermal DSC experiments. The results of other studies, Reference 28, indicate some correlation between the kinetic chemical reaction mechanisms gleaned from DSC experiments and observed energetic material sensitivity as measured from more qualitative macroscopic sensitivity experiments. This correlation is reflected in critical temperature (T_c) differences between energetic materials and their deuterium labeled analogs. Materials whose deuterated analogs possess a higher critical temperature than the unlabeled materials also provide a normal DIE as

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determined by isothermal DSC analysis, and these deuterated materials tend to be more thermally stable. Deuterated materials whose critical temperatures are equal to or less than that of their unlabeled analogs generally correlate with either no DIE or an inverse DIE. The time to explosion curves for BDD and its N-deuterated analog have greater slopes at lower temperatures (approximately 222 to 245°C) than at higher temperatures (approximately 270 to 315°C) with apparent transition periods in between. While there are differences observed between the times to explosion of these two compounds, neither of the compounds exhibits a critical temperature when studied with this experimental technique due to pressure rupture of the sealed sample tube. Even though time to explosion measurements are not as precise as critical temperature measurements, time comparisons along the entire lengths of these curves clearly indicate that the N-deuterated analog exhibits an inverse isotope effect (i.e., it is less thermally stable than the non-deuterated substrate) except in the transition area where no DIE is apparent. DIE values vary between 0.7 and 1.0 with the average value for that section of the curves near the critical temperature (222-230°C) being 0.73. This average value corresponds well with the 0.68 value obtained by extrapolating the isothermal DSC induction period data to this temperature range (see Table 9). Since it has been demonstrated that the presence of atmospheric oxygen in the void above the sample in the sealed DSC sample pans causes a decrease in induction time that results in a more pronounced inverse DIE, time to explosion DIE values were compared with those from isothermal DSC induction period experiments in which the DSC pans were also sealed in air. Based on the above data, it appears the same effect that controls the relatively low pressure, DSC induction period decomposition process in air also controls the more violent time to explosion process.

In order to study the effect of N-deuteration on the thermal explosion for a potential composite explosive, BDD was mixed with varying amounts of an AN/KN mixture. The resulting BAK composites were deuterated specifically at all ammonium sites, and these deuterated composites were subjected to time to explosion tests. For all mixtures, the critical temperatures of the deuterated composites were less than those for the non-deuterated samples, and the   Tc values $(T_{c,h}-T_{c,d})$ were essentially constant (average 11.5°C).

These results are consistent with an inverse isotope effect and suggest that the decomposition mechanism is similar for all the composites. The apparent inverse DIE exhibited by these composites also corresponds well with the results from DSC induction period experiments obtained by using BAK and BAK-d_x (11 mole percent AN) mixtures. The average DIE obtained from samples sealed in air and then heated over the temperature range 195-200°C was 0.48. Since the results from time to explosion tests with AN and AN-d_4 suggest the operation of a normal DIE, it is felt the overall data from these composite tests are consistent with the postulates that the BDD component is decomposing independently of AN, the BDD thermal degradation mechanism plays a significant role in determining time to explosion and critical temperature and the thermal degradation mechanism is similar for all the mixtures. The critical temperature data also shows that the global thermal stability of the BAK mixtures increases with increasing AN concentration. This is consistent with the above postulates in that it is reflective of the high thermal stability of AN and its ultimate participation in the overall degradation process. AN may act as an acidic diluent that inhibits the dissociation of BDD (Equation 1) and in so doing effectively stabilizes the mixture.

An inverse deuterium isotope effect is also reflected in impact data from the BAK composite with 11.0 mole percent AN where the H_{50} value (Reference 15) for the non-deuterated composite was 124 cm and that for the N-deuterated composite was 75 cm. This higher impact sensitivity exhibited by the N-deuterated composite is consistent with DSC induction period results. The decomposition mechanism affecting the DSC induction period, time to explosion and critical temperature apparently also affects the impact sensitivity of the BAK composites. While sample melting is probably not completed during the comparatively rapid impact-initiated decomposition event, local melting at randomly located hot spots may occur. It is conceivable that decomposition will be initiated at these sites with a mechanism similar to that observed from the other experimental conditions.

Impact sensitivity was shown to increase with increasing AN concentration. This trend is consistent with the findings of Kamlet (Reference 29), where an empirical relationship was shown to exist between

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impact sensitivity and oxygen balance for compounds with similar trigger
linkages. Trigger linkage is defined as the weakest atom-to-atom bond. It
was suggested that impact sensitivities of explosives depend on the rates of
the thermal decomposition reaction which occur at the temperatures generated
under the impact hammer, with the rate determining step usually being
homolytic cleavage of the trigger linkage. The DIE results suggest the
trigger linkage resides with the BDD component, probably the $C-NH_3^+$ bond.
When impact sensitivity data from the BAK composites was extrapolated to 100
percent BDD, the H_{50} value matched that impact value obtained from pure BDD.
This further substantiates the correlation between the BAK composite's
behavior to impact and that of pure BDD.

SECTION IV
CONCLUSIONS

It has been shown that BDD decomposes thermally from the molten state via a multistep process that produces a variety of condensed phase and gaseous products. The nature of the products suggest that a proton transfer reaction from cation to anion followed by C-N bond rupture occurs early in the decomposition process. The initial reactions of this process appear to be competitive and may proceed through transient, primary nitramine and nitrosamine species. The presence of early heterocylic reaction products demonstrates that one of the reaction mechanisms involves cycloelimination. The results of a preliminary electron paramagnetic resonance study (Reference 30) suggests the induction period decomposition involves a non-radical (probably ionic) process that is followed by a free-radical oxidation (exothermic) process. Condensed phase induction period studies performed by using specifically deuterated BDD analogs generally displayed inverse deuterium isotope effects. While these studies did not unequivocally reveal the specific covalent bond rupture responsible for generating the conditions favorable for exothermic decomposition, they did provide a direct relationship between induction period chemistry as measured by quantitative isothermal differential scanning calorimetry and macroscopic thermal sensitivity properties. The DIE results suggest that

a. The same effect that plays a significant role in controlling the relatively low pressure DSC induction period of the BDD thermal degradation process in air also plays a similar role in the more violent time to explosion process.

b. BDD, when formulated into BAK composites of varying BDD concentration, decomposes independently of the AN/KN components always by a process similar to that of pure BDD.

c. Reactions occurring during the induction period of the BDD thermal degradation process also play a significant role in controlling the DSC induction period, times to explosion, critical temperatures and impact sensitivities of BAK composites.

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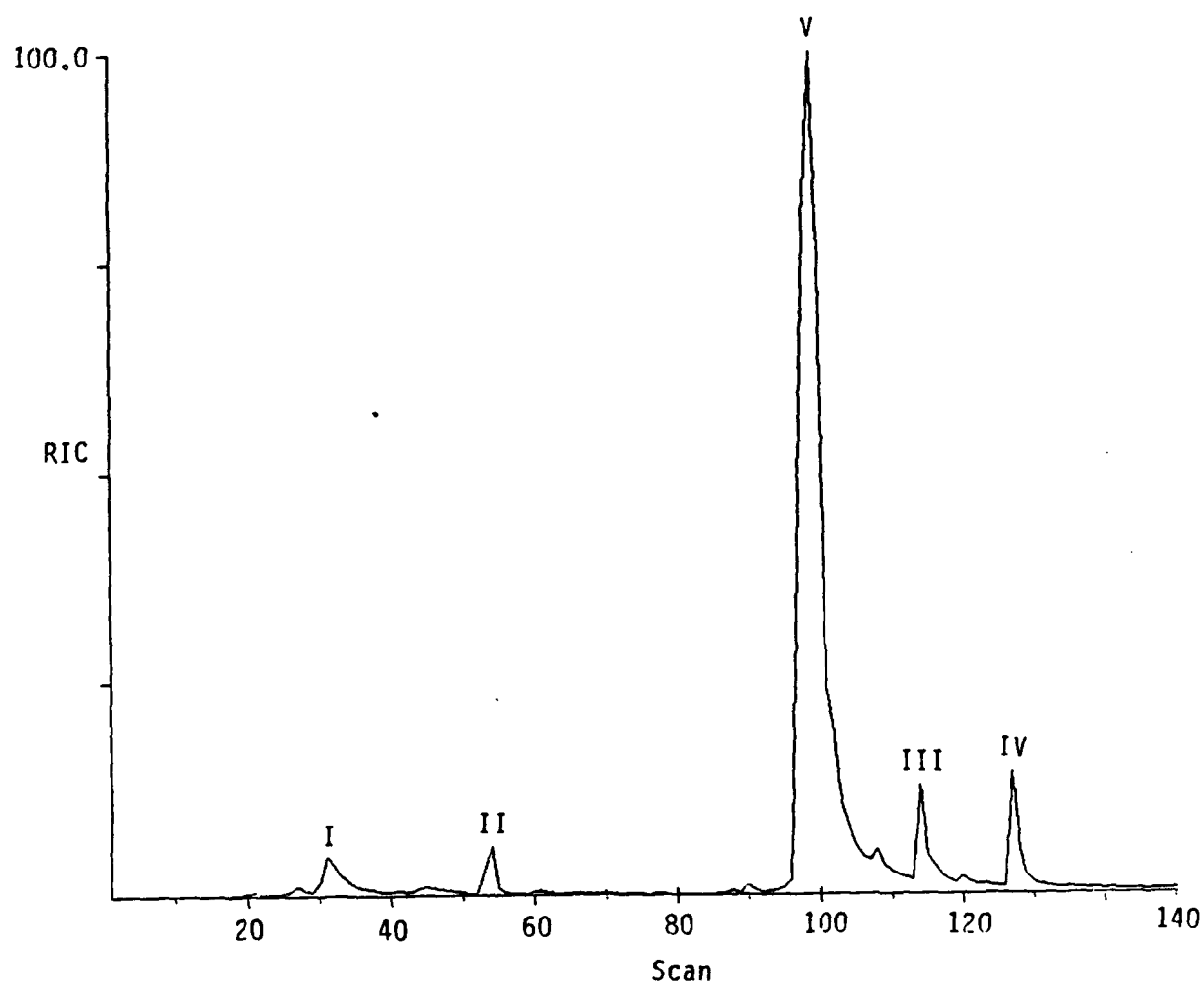
Figure 1. Reconstructed Ion Chromatogram of BDD Decomposition Products
From Isothermal TGA Experiment II

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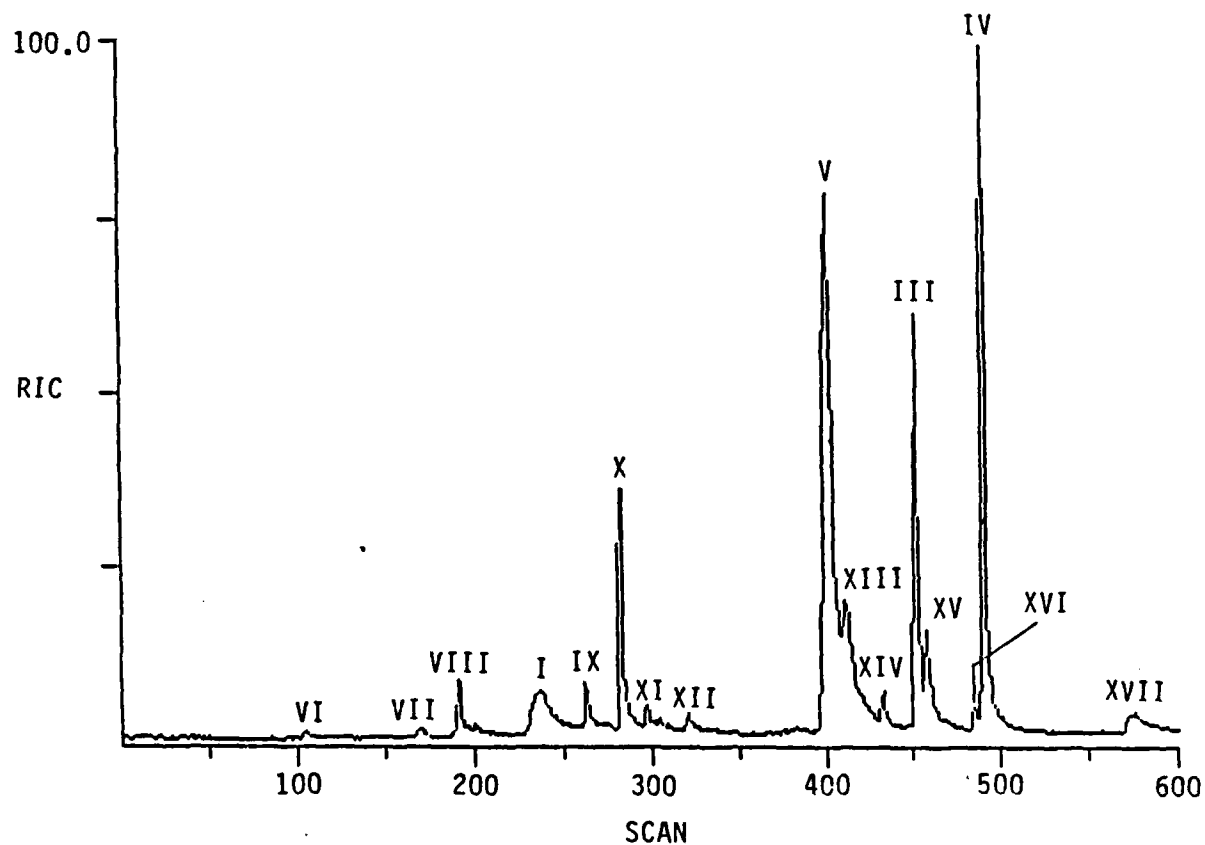
Figure 2. Reconstructed Ion Chromatogram of BDD Decomposition Products From Isothermal DSC Experiment

SAMPLE VIII
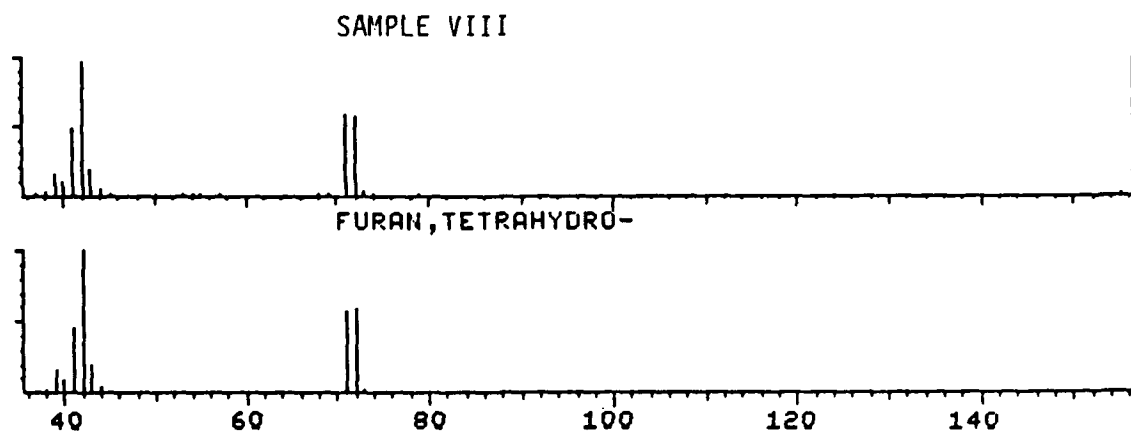
FURAN,TETRAHYDRO-

Figure 3. EI Mass Spectrum of Compound VIII Compared to That of
Tetrahydrofuran

SAMPLE XV

PYRROLIDINE,1-NITRO-
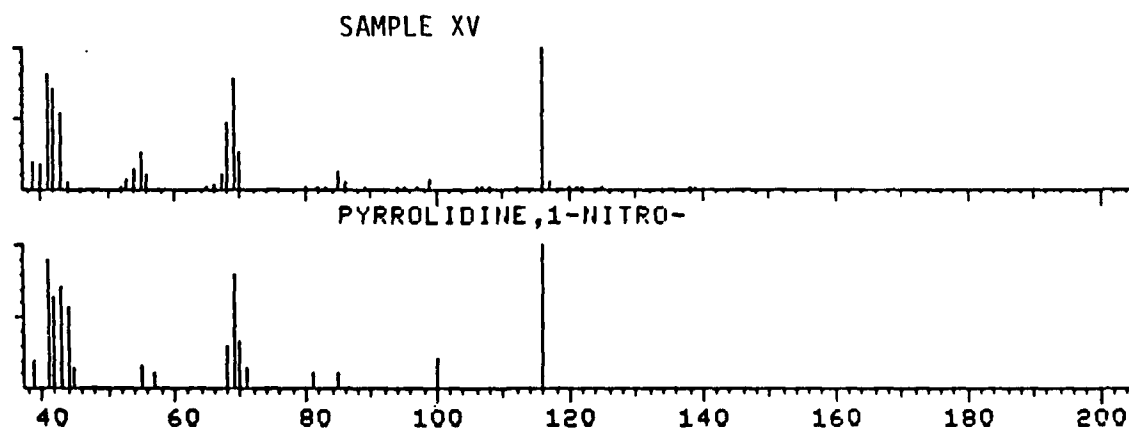
Figure 4. EI Mass Spectrum of Compound XV Compared to That of
N-nitropyrrolidine

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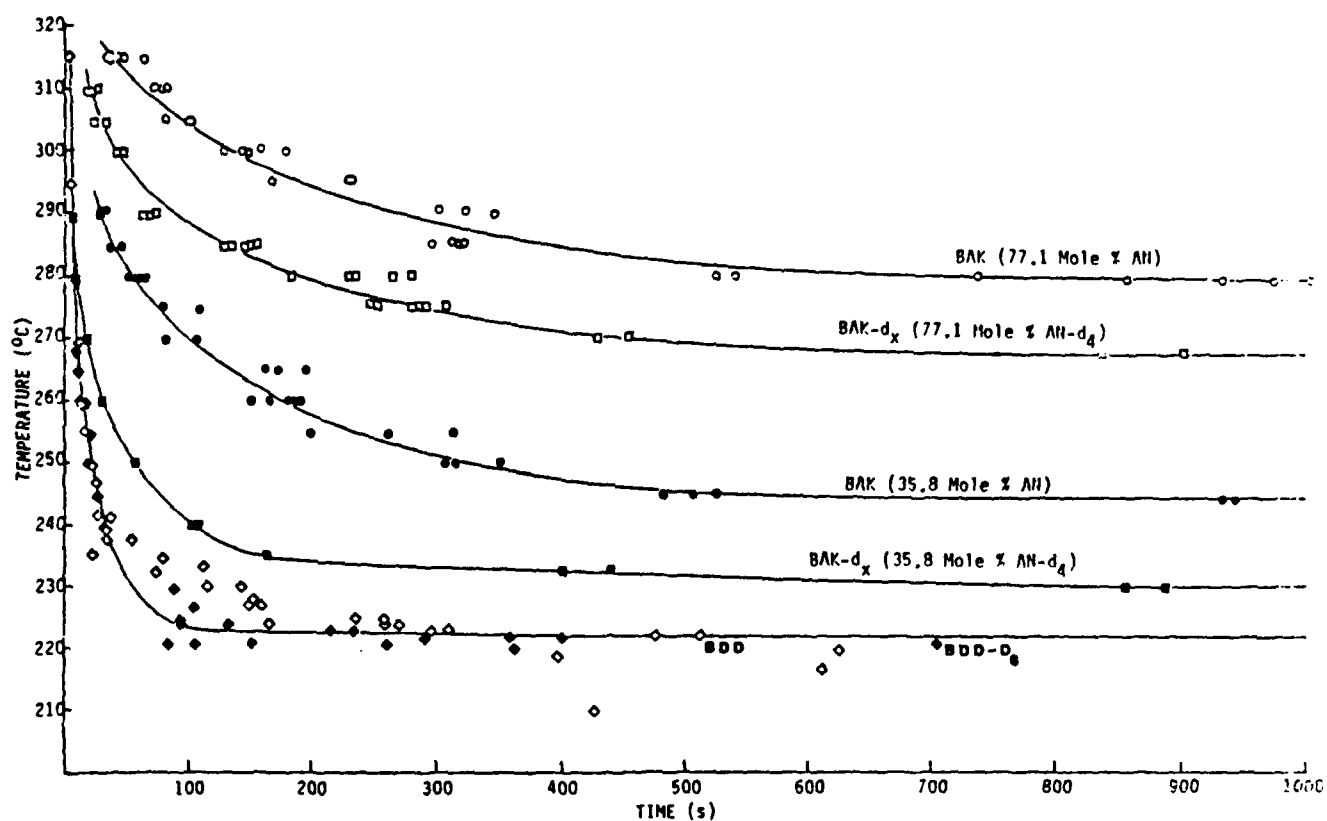
Figure 5. Experimental Time to Explosion Curves for BDD, BAK (35.8 Mole Percent AN), BAK (77.1 Mole Percent AN) and Their N-Deuterated Analogs
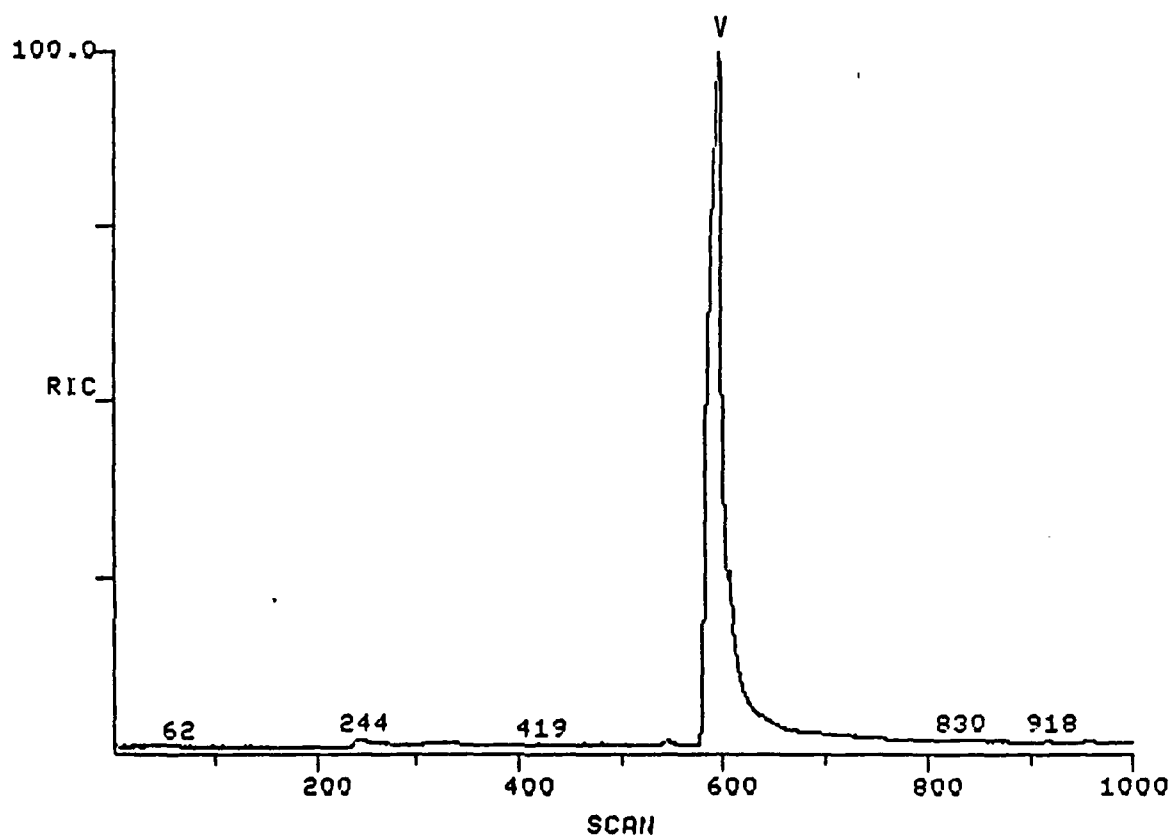
Figure 6. Reconstructed Ion Chromatogram of PN Decomposition Products

TABLE 1. MASS SPECTRAL DATA FOR PRODUCTS I–V

Original Salt	Product	m/e (tentative assignment)	Type Expt
BDD	I $M=69$	70[base] (M+H) 84 98(M+(C$_2$H$_5$)) 110(M+C$_3$H$_5$)	CI/CH$_4$
		71[base] (M+D) 103(M+C$_2$D$_5$)	CI/CD$_4$
BDD	II $M=98$	71 76 99[base](M+H) 127(M+C$_2$H$_5$) 139(M+C$_3$H$_5$)	CI/CH$_4$
BDD	III	71 73 76(CH$_2$NO$_3$) 88 101 118[base](M-NO$_3$) 181(M+H)	CI/CH$_4$
BDD	$M=180$	71 73 76(CH$_2$NO$_3$) 88 102 118[base](M-NO$_3$) 181(M+H)182(M+D)	CI/CD$_4$
BDD-1,1,4,4-d$_4$	$M=184$	73 74[base] 75 76(CH$_2$NO$_3$) 90 101 122(M-NO$_3$) 185(M+H)	CI/CH$_4$
BDD-2,2,3,3-d$_4$	$M=184$	73 74 76(CH$_2$NO$_3$) 92 104 121 122[base](M-NO$_3$) 185(M+H)	CI/CH$_4$
BDD		43 46[base](NO$_2$) 71 73 76(CH$_2$NO$_3$) 90(C$_2$H$_4$NO$_3$)	EI[a]
BDD-1,1,4,4-d$_4$		46[base](NO$_2$) 78(CD$_2$NO$_3$) 92(C$_2$H$_2$D$_2$NO$_3$)	EI
BDD-2,2,3,3,-d$_4$		46[base](NO$_2$) 76(CH$_2$NO$_3$) 90(C$_2$D$_2$H$_2$NO$_3$)	EI
Predicted	1,3-DNBu	46 76 90	EI

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TABLE 1. MASS SPECTRAL DATA FOR PRODUCTS I-V (CONCLUDED)

Original Salt	Product	m/e (tentative assignment)	Type Expt
BDD	IV	71[base] 73 76(CH_2NO_3) 88 101 118(M-NO_3) 181(M+H)	CI/CH_4
BDD	M-180	71[base] 76(CH_2NO_3) 118(M-NO_3) 181(M+H) 182(M+D)	CI/CD_4
BDD-1,1,4,4-d_4	M-184	74[base] 89 122(M-NO_3) 185(M+H)	CI/CH_4
BDD-2,2,3,4-d_4	M-184	74 75[base] 76 92 122(M-NO_3) 185(M+H)	CI/CH_4
BDD		46[base](NO_2) 76(CH_2NO_3)	EI[b]
BDD-1,1,4,4-d_4		46[base](NO_2) 78(CD_2NO_3)	EI
BDD-2,2,3,3-d_4		46[base](NO_2) 76(CH_2NO_3)	EI
Authentic Sample	1,4-DNBu	46 76	
BDD	V	70 84 101[base](M+H) 129(M+C_2H_5) 141(M+C_3H_5)	CI/CH_4
BDD	M=100	102[base](M+D) 134(M+C_2D_5) 146(M+C_3D_5)	CI/CD_4
BDD		39 41[base] 42 43 68 69 100(M)	EI[c]
Authentic Sample	PNSA	39 41[base] 42 43 68 69 100	

a. Spectrum consistent with ion fragment pattern expected from 1,3-dinitratobutane (1,3-DNBu)

b. Spectrum consistent with ion fragment pattern for authentic 1,4-dinitratobutane (1,4-DNBu)

c. Spectrum consistent with ion fragment pattern for authentic N-nitrosopyrrolidine (PNSA)

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TABLE 2. MASS SPECTRAL (EI) DATA FOR PRODUCT X (4-NITRATO-1-BUTENE)

Source		m/e (tentative assignment)		
BDD	39 41[base](CH_2CHCH_2)	46(NO_2)	55($CH_2CHCH_2CH_2$)	76(CH_2ONO_2)
Predicted	41	46	55	76
BDD-1,1,4,4-d_4	40 41 42 43 (CD_2CHCH_2)	46[base](NO_2)	59($CD_2CHCH_2CD_2$)	78(CD_2ONO_2)
Predicted	41 43	46	59	78
BDD-2,2,3,3-d_4	40 41 42 43 44(CH_2CDCD_2)	46[base](NO_2)	58($CH_2CDCD_2CH_2$)	76(CH_2ONO_2)
Predicted	44	46	58	76

TABLE 3. MASS SPECTRAL (CI) DATA FOR PRODUCT X (4-NITRATO-1-BUTENE)

Source		m/e (tentative assignment)		
BDD	71[base]($CH_2CHCH_2CH_2O$)	76(CH_2ONO_2)	87($C_4H_7O_2$)	118(Molecular ion+H)
BDD-1,1,4,4-d_4	75	78[base]	90	122
BDD-2,2,3,3-d_4	74	76[base]	90	121

TABLE 4. MASS SPECTRAL DATA FOR PRODUCTS VIII, XIV AND XV

ID #	COMPOUND	MW	MS/(CI/CH$_4$)	
VIII	Tetrahydrofuran	72	73(M+H)	101(M+C$_2$H$_5$)
XIV	2,3-dinitratobutane	180	181(M+H)	
XV	N-nitropyrrolidine	116	117(M+H)	

TABLE 5. PRODUCTS IDENTIFIED FROM BDD THERMOLYSIS RESIDUE

Product #	Product Name
III	1,3-dinitratobutane
IV	1,4-dinitratobutane
V	N-nitrosopyrrolidine
VIII	tetrahydrofuran
X	4-nitrato-1-butene
XIV	2,3-dinitratobutane
XV	N-nitropyrrolidine

TABLE 6.   ION CHROMATOGRAPHY DATA FROM BDD THERMOLYSIS RESIDUE

Sample	Observation	NO_3^-	NH_4^+	$\overline{CH_2CH_2CH_2CH_2NH_2}^+$
1.	Not heated	1.00	0.0000	0.000
2.	Sample splattered on top of bulb turned dark yellow	1.05	<0.0001	0.000
3.	Liquid in bottom of bulb turned yellow and started to bubble	1.05	<0.0001	0.000
4.	Liquid in bottom turned red-brown and bubbled vigorously	1.00	0.0001	0.002
5.	Liquid in bottom turned dark brown, no further evidence of reaction	0.35	0.0004	0.006

TABLE 7.   IMPACT SENSITIVITY DATA FOR BDD-BASED COMPOSITES

Composite/Compound	OB_{100}	$H_{50}(cm)$[1]
BAK (11.0 mole % AN)	-4.21	124
BAK (35.8 mole % AN)	-2.96	82
BAK (55.2 mole % AN)	-1.62	100
BAK (77.1 mole % AN)	+0.99	49
BDD	-4.67	128
BAK-d_x (11.0 mole % AN-d_4)	-4.21	75

1.   Reference 15

TABLE 8.   CRITICAL TEMPERATURE DATA FOR BAK/BAD-dx COMPOSITES

Composite/Compound	Critical Temperature (^{O}C)
BDD	<222[1]
BDD (N-deuterated)	<222[1]
BAK (11.0 mole % AN)	239
BAK-d_x (11.0 mole % AN-d_4)	230
BAK (35.8 mole % AN)	244
BAK-d_x (35.8 mole % AN-d_4)	230
BAK (55.2 mole % AN)	264
BAK-d_x (55.2 mole % AN-d_4)	253
BAK (77.1 mole % AN)	279
BAK-d_x (77.1 mole % AN-d_4)	267

1. Critical temperature could not be determined.

TABLE 9. DSC INDUCTION PERIOD DEUTERIUM ISOTOPE EFFECTS FOR BDD AND BAK(11 mole % AN) AND THEIR DEUTERATED ANALOGS IN AIR AND NITROGEN ATMOSPHERES

t_d/t_h

Temp (°C)	BDD- N,N,N',N',N'-d_6		BDD- 1,1,4,4-d_4		BDD- 2,2,3,3-d_4		BAK-d_x (11 mole % AN)
	air	N_2	air	N_2	air	N_2	air
175	0.74 ± 0.12	---	---	---	---	---	---
180	0.85 ± 0.15	---	---	---	0.47 ± 0.05	---	---
185	0.69 ± 0.10	---	---	---	---	---	---
190	0.70 ± 0.04	---	0.52 ± 0.03	---	---	---	---
191	0.75 ± 0.16	---	---	---	---	---	---
195	0.72 ± 0.12	---	0.55 ± 0.07	---	---	---	0.51 ± 0.05
198	---	---	---	---	---	---	0.47 ± 0.08
200	0.70 ± 0.11	---	0.55 ± 0.08	---	0.25[1]	---	0.45 ± 0.08
215	0.68[1,2]	0.98 ± 0.08	0.59[1]	0.81 ± 0.07	---	0.18 ± 0.01	0.43[1]

1. Calculated values
2. Extrapolated to the 222-230°C range

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TABLE 10. COMPARISON OF CUMULATIVE AND NON-CUMULATIVE INDUCTION PERIOD
TIMES FOR BDD IN AIR AT 190 C°

| Exp't | Induction Period (min.) | | |
	Segment 1	Segment 2	Total
1	3.73	3.87	7.60
2	3.73	3.88	7.61
3	4.35	3.54	7.89
		Average	7.70
4	7.70±0.76		7.70±0.76

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